

**PATENT APPLICATION**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of

Piotr KULA et al.

Group Art Unit: 1793

Application No.: 10/531,477

Examiner: W. ZHU

Filed: April 15, 2005

Docket No.: 122041

For: METHOD FOR UNDER-PRESSURE CARBURIZING OF STEEL WORKPIECES

**DECLARATION UNDER 37 C.F.R. §1.132**

I, Dr. Piotr Kula, a citizen of Poland, hereby declare and state:

1. I have a degree in mechanical engineering, materials science and heat treating of metals which was conferred upon me by Politechnika Lodzka (Poland) in 1975.
2. I have been employed by Politechnika Lodzka since 1975 (since 1996 as professor), and I have had a total of 20 years experience in the field of steel carburizing.
3. I am a named inventor in the above-captioned patent application. I am familiar with the patent application.
4. I have a professional relationship with the Assignees, Seco/Warwick SP.ZO.O. and Politechnika Lodzka, of the above-identified patent application. In the course of that professional relationship, I received compensation for my work relating to research and development regarding steel carburization. I am not being specially compensated for my work in preparing this Declaration.
5. I and/or those under my direct supervision and control have conducted the following experiments in accordance with good laboratory practices.

6. I and/or those under my direct supervision and control have conducted the following experiments.

The following experimental results demonstrate that the presently claimed method for under-pressure carburizing steel achieves unexpected results by restraining the austenite grain growth on the surface of the charge, while avoiding the formation of undesirable iron nitrides on the surface of the charge, when the active nitrogen carrier (e.g., ammonia) is (1) introduced into the vacuum furnace chamber during the preheating of the charge after the charge reaches 400°C (i.e., the lower limit) and (2) continuously introduced until the charge reaches the carburizing temperature, at which point the active nitrogen carrier is stopped and the carbon carrier introduction is begun (i.e., the upper limit).

For the following experiments, 1000°C was selected as the carburizing temperature, and is thus referred to below as the upper limit for purposes of Experiments 1-8.

#### THE LOWER LIMIT

Experiments 1-5 were conducted on two different low carbon steel grade charges at five different process conditions to confirm that the introduction of a nitrogen carrier only after a charge reaches a temperature of 400°C (i.e., the lower limit) unexpectedly inhibits austenite grain growth.

The first low carbon steel grade charge was comprised of 16MnCr5. The second low carbon steel grade charge was comprised of 18CrNiMo7-6. Each of the low carbon steel grade charges were treated in a 200 x 200 x 400 mm low-pressure vacuum furnace chamber at different process conditions.

The five sets of process conditions were labeled as: Experiment 1, Experiment 2, Experiment 3, Experiment 4 and Experiment 5. Experiment 1 consisted of conventional under-pressure carburizing without any introduction of ammonia gas during preheating of the charge to the carburizing temperature. Experiment 2 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 20°C - 400°C (i.e., starting below the lower limit).

Experiment 3 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 400°C - 1000°C (i.e., representative of the claimed process).

Experiment 4 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 20°C - 1000°C (i.e., starting below the lower limit and continuing until the upper limit).

Experiment 5 consisted of under-pressure carburizing with the nitrogen carrier in the temperature interval of 360°C - 1000°C (i.e., starting slightly below the lower limit and continuing until the upper limit). The remaining parameters for Experiments 1-5 were kept constant and are summarized below in Table 1.

Table 1: Process Parameters for Experiments 1-5

Parameter	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5
Ammonia Dosing Temperature Range	-	20°C - 400°C	400°C - 1000°C	20°C - 1000°C	360°C - 1000°C
Ammonia Flow	-	50 L/hr	50 L/hr	50 L/hr	50 L/hr
Ammonia Pressure	-	26 mbar	26 mbar	26 mbar	26 mbar
Temperature Of Carburizing	1000°C	1000°C	1000°C	1000°C	1000°C
Time Of Boost	20 min	20 min	20 min	20 min	20 min
Time Of Diffusion	5 min	5 min	5 min	5 min	5 min
Acetylene Flow	72.9 L/hr	72.9 L/hr	72.9 L/hr	72.9 L/hr	72.9 L/hr
Ethylene Flow	72.9 L/hr	72.9 L/hr	72.9 L/hr	72.9 L/hr	72.9 L/hr
Hydrogen Flow	124.2 L/hr	124.2 L/hr	124.2 L/hr	124.2 L/hr	124.2 L/hr
Pressure	3 - 8 mbar	3 - 8 mbar	3 - 8 mbar	3 - 8 mbar	3 - 8 mbar
Charge Area	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>

After treatment under the process conditions of Experiments 1-5, the austenite mean grain diameter was measured for each of the two steel grades (i.e., 16MnCr5 and 18CrNiMo7-6).

The austenite mean grain diameter was determined in accordance with ASTM E1383-97 by using professional software for a quantitative metallography, which is common method for determining grain diameter. The results are summarized below in Table 2.

Table 2: Mean Austenite Grain Diameter of Under-Pressurized Steel Charges According to ASTM E1382-97

Mean Grain Diameter ASTM E1382-97	18CrNiMo7-6		16MnCr5	
	Mean Grain Diameter	Increase in Grain Diameter Compared to Experiment 3	Mean Grain Diameter	Increase in Grain Diameter Compared to Experiment 3
Experiment 1	26.2 $\mu\text{m}$	154.4%	18.5 $\mu\text{m}$	18.6%
Experiment 2	26.2 $\mu\text{m}$	154.4%	19.2 $\mu\text{m}$	23.1%
Experiment 3	10.3 $\mu\text{m}$	0%	15.6 $\mu\text{m}$	0%
Experiment 4	13.1 $\mu\text{m}$	27.2%	17.3 $\mu\text{m}$	10.9%
Experiment 5	12.7 $\mu\text{m}$	23.3%	17.3 $\mu\text{m}$	10.9%

The microstructures for each of the two treated steel grades treated under the process parameters for Experiments 1-5 were etched with Mi7Fe to visually detect the austenite grains on the surface of the steel charges using SEM and EDS techniques. The microstructures for Experiments 1-5 are illustrated below in Figures 1-2, respectively.

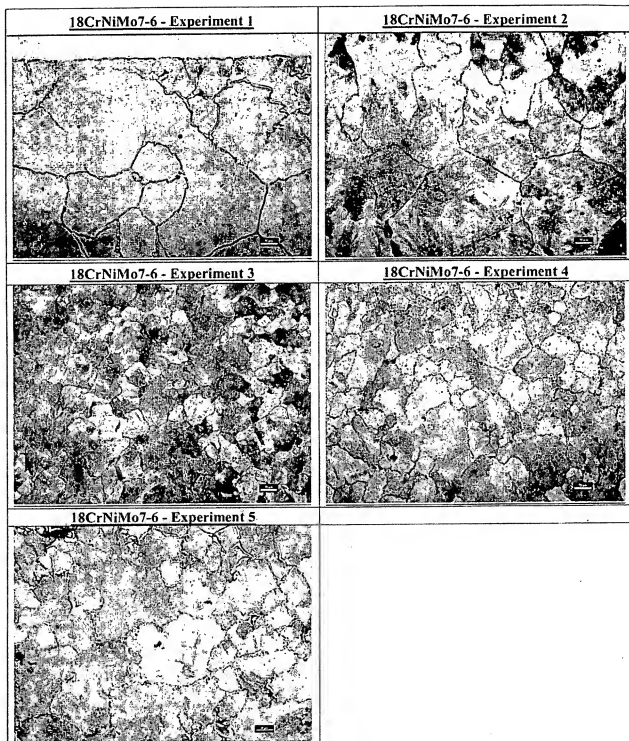


Figure 1: Microstructure for 18CrNiMo7-6 Steel Treated Under Experiments 1-5

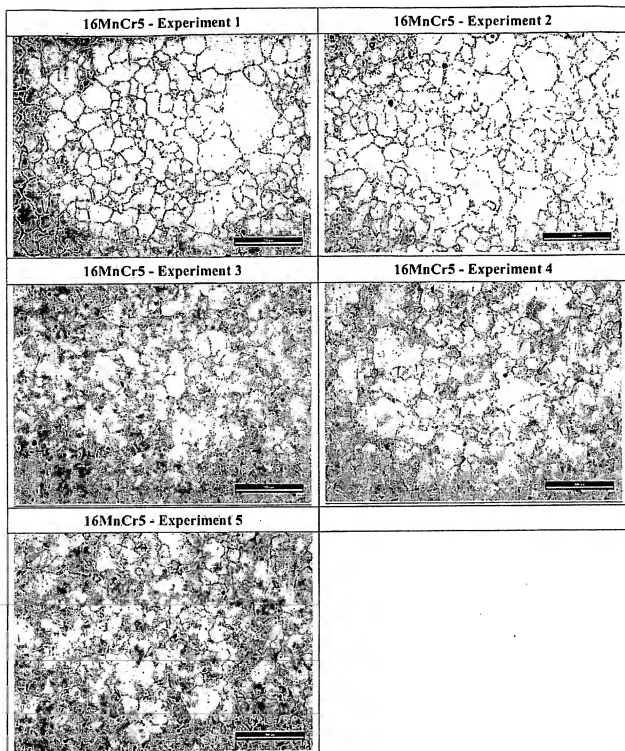


Figure 2: Microstructure for 16MnCr5 Steel Treated Under Experiments 1-5

As shown above in Table 2 and visually confirmed by Figures 1-2, the steel charges that were subjected to Experiment 3 (i.e., the claimed method) possessed the finest austenite mean grain diameter (10.3  $\mu\text{m}$  for the 18CrNiMo7-6 charge and 15.6  $\mu\text{m}$  for the 16MnCr5 charge). Furthermore, as shown above in Table 2, Experiment 5 increased the austenite mean grain diameter by at least 23.3% for the 18CrNiMo7-6 charge and by at least 10.9% for the 16MnCr5 charge.

As such, the experimental results demonstrate that the presently claimed method for under-pressure carburizing a steel charge mixture by introducing an active nitrogen carrier into the vacuum furnace chamber during the preheating of the charge after the charge reaches 400°C unexpectedly restrained the austenite grain growth on the surface of the steel charge while avoiding the formation of undesirable iron nitrides that adversely affect the microstructure of the charge.

#### THE UPPER LIMIT

Experiments 6-8 were conducted to confirm that continuously introducing the nitrogen carrier (i.e., ammonia gas) from at least 400°C until the steel charge reaches the carburizing temperature, at which point the nitrogen carrier is stopped and the carbon carrier introduction is begun, unexpectedly restrains the growth of austenite grains on the steel charge, while avoiding the formation of undesirable iron nitrides on the surface of the charge.

Experiment 6 consisted of "prenitriding", i.e., introducing the nitrogen carrier beginning at 400°C into a low-pressure vacuum furnace chamber containing a 18CrNiMo7-6 charge. The ammonia gas was continuously introduced into the vacuum furnace chamber for 70 minutes until the temperature of the steel charge was 750°C, a temperature less than the carburizing temperature (1000°C). At this point, the flow of the nitrogen carrier was stopped and the charge was heated to the carburizing temperature of 1000°C under vacuum. The carbon carrier was then introduced when the charge reached 1000°C. The steel charge was then quenched and etched with MilFe (Nital).

Experiment 7 consisted of "prenitriding", i.e., introducing the nitrogen carrier beginning at 400°C into a low-pressure vacuum furnace chamber containing a 18CrNiMo7-6 charge. The nitrogen carrier was continuously introduced into the vacuum furnace chamber for 120 minutes until the temperature of the steel charge reached the carburizing temperature of 1000°C. At this point, the flow of the nitrogen carrier was stopped and the introduction of the carbon carrier began. As with Experiment 6, the steel charge was then quenched and etched with MilFe (Nital). Experiment 7 corresponds to the process recited in the present claims.

Experiment 8 consisted of "prenitriding", i.e., introducing the nitrogen carrier beginning at 400°C into a low-pressure vacuum furnace chamber containing a 18CrNiMo7-6 charge. The nitrogen carrier was continuously introduced into the vacuum furnace chamber for 120 minutes until the temperature of the steel charge reached the carburizing temperature of 1000°C. At this point, the introduction of the carbon carrier began and was not stopped until the carburization was completed. However, the introduction of the nitrogen carrier also did not stop when the steel charge reached the carburizing temperature, but was introduced for an additional 10 minutes (130 minutes total). As with Experiments 6 and 7, the charge was then quenched and etched with MilFe (Nital).

The process parameters for Experiments 6-8 are summarized below in Table 3.



Table 3: Process Parameters for Experiments 6-8

Parameter	Experiment 6	Experiment 7	Experiment 8
Ammonia Dosing Temperature Range	400°C - 750°C	400°C - 1000°C	400°C - 1000°C
Ammonia Flow	50 L/h	50 L/h	50 L/h
Ammonia Pressure	26 mbar	26 mbar	26 mbar
Total Ammonia Dosing Time	70 min	120 min	130 min
Heating Rate of Steel Charge	5 °C/min	5 °C/min	5 °C/min
Temperature of Carburizing	1000°C	1000°C	1000°C
Time of Boost	20 min	20 min	20 min.
Time of Diffusion	5 min	5 min	5 min
Acetylene Flow	72.9 L/h	72.9 L/h	72.9 L/h
Ethylene Flow	72.9 L/h	72.9 L/h	72.9 L/h
Hydrogen Flow	124.2 L/h	124.2 L/h	124.2 L/h
Pressure	3 – 8 mbar	3 – 8 mbar	3 – 8 mbar
Charge Area	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>	0.4 m <sup>2</sup>
Cooling (Nitrogen) Pressure	12 bar	12 bar	12 bar

After treatment under the process conditions of Experiments 6-8, the average retained austenite content was measured in the 18CrNiMo7-6 charge. The average retained austenite content was determined by using specialized software to quantitatively measure the white fraction of austenite in five different locations on each 18CrNiMo7-6 charge and calculating the mean of the sample. The results are summarized below in Tables 4-5 and Figure 3, respectively.

Table 4: Comparison of Average Retained Austenite Content in Experiments 6 and 7

Experiment	Total Time of Ammonia Flow	Average Retained Austenite Content	Increase in Retained Austenite Content
Experiment 6	70 min	6.41 %	3.4 %
Experiment 7	120 min	6.63 %	

Table 5: Comparison of Average Retained Austenite Content in Experiments 7 and 8

Experiment	Total Time of Ammonia Flow	Average Retained Austenite Content	Increase in Retained Austenite Content
Experiment 7	120 min	6.63 %	42.4 %
Experiment 8	130 min	9.44 %	

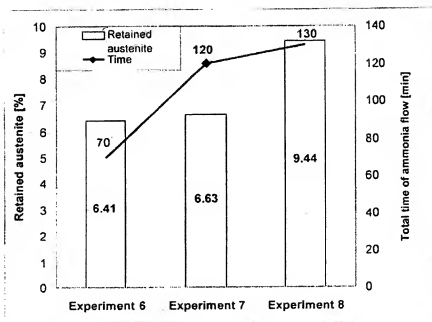
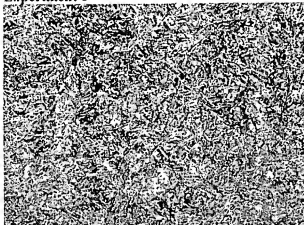


Figure 3: Comparison of retained austenite content in charge, and total ammonia dosing time for Experiments 6-8.

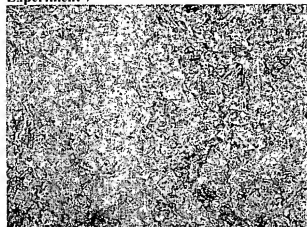
The microstructures for the steel grade treated under the process parameters for Experiments 6-8 were etched with MilFe to visually detect the retained austenite on the surface of the steel

charges using SEM and EDS techniques. The microstructures for Experiments 6-8 are illustrated below in Figure 4, respectively.

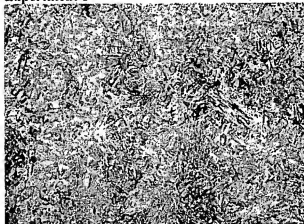
Experiment 6



Experiment 7



Experiment 8



**Figure 4: Microstructures Of 18CrNiMo7-6 Steel Treated Under Experiments 6-8**

As shown above in Table 4 and Figures 3-4, introducing the nitrogen carrier under the process parameters of Experiment 6 (i.e., 400°C - 750°C for 70 minutes) compared to introducing the nitrogen carrier under the process parameters of Experiment 7 (i.e., 400°C - 1000°C for 120 minutes) resulted in only a 3.4 % increase in the retained austenite content charge. As such, comparing the results of Experiments 6-7 demonstrates that the nitrogen carrier may be dosed during the entire preheating stage (i.e., until the charge reaches carburizing temperature and a

carbon carrier is introduced) without significantly increasing (i.e., 3.4 %) the retained austenite content on the surface of the steel charge.

However, as shown above in Table 5 and Figures 3-4, introducing the nitrogen carrier under the process parameters of Experiment 8 (i.e., 400°C - 1000°C for 130 minutes, or an additional 10 minutes after the charge reached the carburizing temperature) compared to the process parameters of Experiment 7 resulted in a 42.4% increase in the retained austenite content on the surface of the steel charge. As such, comparing the results of Experiments 7-8 demonstrates that extending the introduction of the nitrogen carrier after the steel charge reaches the carburizing temperature by only 10 minutes while introducing the carbon carrier, significantly increases (i.e., 42.4 %) the retained austenite content on the surface of the steel charge.

As such, the experimental results demonstrate that the presently claimed method for under-pressure carburizing a steel charge mixture by continuously introducing the nitrogen carrier from at least 400°C to until the charge reaches the carburizing temperature unexpectedly restrained the austenite grain growth on the surface of steel charge while avoiding the formation of undesirable iron nitrides that adversely affect the microstructure of the charge.

7. I hereby declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine and/or imprisonment under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing therefrom.

Date:

12.12.2008Dr. Piotr KULA